Quantum-Classical Connection for Hydrogen Atom-like Systems

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Abstract
The Bohr-Sommerfeld quantum theory specifies the rules of quantization for circular and elliptical orbits for a one-electron hydrogen atom–like system. This article illustrates how a formula connecting the principal quantum number '*n*' and the length of the major axis of an elliptical orbit may be arrived at starting from the quantum mechanical description and how in the limit when '*n*' is large one gets the expected classical result.
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Introduction

According to the non-relativistic version of quantum mechanics, the energy of the electron in a hydrogen-like atom depends only on the principal quantum number n (apart from the atomic number Z of the nucleus.) Again, in non-relativistic classical mechanics, the energy of such a particle, which describes an elliptical path that keeps the nucleus at one focus, depends only on the size ($2a$) of the major axis. As one expects to recover the classical result in the large n limit of quantum mechanics ('the correspondence principle'), there ought to be a connection between n and $2a$. This connection will be examined in this article. We begin by recalling the salient features of the two approaches:
The classical orbits under inverse-square type force ('Keplerian orbits'):
The following quantities remain conserved (Rana and Joag, 1991; Synge and Griffith, 1959):

1. Energy, which depends only on the size of the major axis:

$$E = -\frac{Ze^2}{2a} \qquad (1)$$

2. Angular momentum vector;
3. Runge-Lenz vector, which gives the direction of the major axis.

Hydrogen-like atom in quantum mechanics (Ghatak and Lokanathan, 1984):
The wave function (ignoring spin) of the system :

$$\Psi_{nlm}(r,\theta,\phi) = NR_{nl}(r)Y_{lm}(\theta,\phi) \qquad (2)$$

where N is a normalization constant, while

$$Y_{lm}(\theta,\phi) = (-1)^m . \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right]^{1/2} .[(1-x^2)^{m/2} . \frac{1}{2^l l!} . \frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l]e^{im\phi} \ (m \geq 0) \qquad (3)$$

x standing for $cos\theta$; and

$$Y_{lm}(\theta,\phi) = (-1)^m Y^*{}_{l,-m}(\theta,\phi) \quad (m<0) \qquad (4)$$

The radial part of the wave function reads

$$R_{nl}(r) = e^{-\frac{\rho}{2}} .\rho^l .L_{n+l}^{2l+1}(\rho) \qquad (5)$$

$L_{n+l}^{2l+1}(\rho)$ being an associated Laguerre polynomial (Ghatak and Lokanathan, 1984) with

$$\rho = 2\eta r \qquad (6)$$

$$\eta = \sqrt{\frac{2\mu|E|}{\hbar^2}} \qquad (7)$$

E being the energy (E< 0) and μ the reduced mass of the system. The quantum numbers *n, l, m* have their usual meanings.

Eigenvalue of energy (E) of bound states is given by

$$E = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} \qquad (8)$$

while

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+1} . \frac{[(n+l)!]^2 \rho^k}{(n-l-1-k)!(2l+1+k)!k!} \qquad (9)$$

We are looking for the classical limit of the quantum mechanical solution. This requires that we take a large value for n. (Also large Z, which, however, is a constant for a given system.) But something else is also to be taken into account. In classical mechanics all three components of angular momentum have well-defined values. There is also a vector (Runge-Lenz vector) which points in the direction of the major axis; we shall come to this later. As the operators that correspond to the components of angular momentum (orbital angular momentum) do not commute with each other, only one component (z-component, by convention) of angular momentum and the magnitude of the angular momentum have, simultaneously, definite values in quantum mechanics.

Now, writing the orbital angular momentum as $\vec{l}\hbar$, we have

$$\left\langle \hat{l}_x{}^2 \right\rangle + \left\langle \hat{l}_y{}^2 \right\rangle + \left\langle \hat{l}_z{}^2 \right\rangle = \left\langle (\hat{l}^2) \right\rangle = l(l+1) \qquad (10)$$

where $\langle \hat{A} \rangle$ stands for the expectation value of the operator $\hat{A}$. Now

$$\langle \hat{l}_z \rangle = m \ (\ -l \leq \ m \leq \ l \ ) \qquad (11)$$

with

$$\langle \hat{l}_x \rangle = \langle \hat{l}_y \rangle = 0 \qquad (12)$$

If $\langle \hat{l}_z \rangle = \pm l$, then $\langle \hat{l}_z{}^2 \rangle = l^2$, and

$$\langle \hat{l}_x{}^2 \rangle + \langle \hat{l}_y{}^2 \rangle = l \qquad (13)$$

i.e.

$$(\Delta l_x)^2 + (\Delta l_y)^2 = l \qquad (14),$$

Δl_x, Δl_y being the standard deviations of l_x, l_y ; so that the relative uncertainty in the direction of the angular momentum is small. Conversely, if $\langle \hat{l}_z \rangle = 0$, then $\langle \hat{l}_x{}^2 \rangle + \langle \hat{l}_y{}^2 \rangle = l(l+1)$; the direction of the angular momentum is now totally uncertain. Clearly the classical situation corresponds to $\langle \hat{l}_z \rangle = \pm l$. For concreteness we shall take $\langle \hat{l}_z \rangle = l$. As a matter of fact, we shall consider only large values of l. Notice now that $m = \langle \hat{l}_z \rangle = l$ implies

$$|Y_{lm}(\theta,\phi)|^2 \rightarrow (1-x^2)^l \qquad (15)$$

and, for large values of l, this quantity is practically equal to zero except when $x = 0$ or $\theta = \pi/2$, i.e.on the XY plane (Pauling and Wilson, 1935; Roy, 2010). The electron therefore spends most of its time on the XY plane: the first hint of the emergence of a circular or an elliptical orbit in the classical limit.

Connection between 'n' and the length of the major axis

We shall next find the most probable value of r for the electron; this requires finding the value of r (or the values of r) at which $R_{nl}^2 r^2$ has a local maximum (maxima.) The cases $l = n-1, n-2, n-3, n-4$ can be handled analytically. (Abel's theorem rules out the possibility of solving equations of degree higher than four by algebraic techniques (Hall and Knight, 1969).

The case *l* = *n-1*

Here

$$R_{nl}^2 r^2 \rightarrow e^{-\rho} \rho^{2n} \qquad (16)$$

and maximization of $R_{nl}^2\, r^2$ through demanding that $\frac{d}{d\rho}\left(R_{nl}^2 r^2\right) = 0$ gives $\rho = 2n$. Using this value of ρ (or, rather $r = \frac{\rho}{2\eta}$) in the classical formula for the energy E (for a circular orbit) viz. $E = -\frac{Ze^2}{2r}$, we get

$$E = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} \qquad (17)$$

this is precisely Bohr's formula.

Let us work out the width of the distribution of $e^{-\rho}\rho^{2n}$ around the maximum. Putting ρ = $2n + \alpha$, and assuming that $\alpha << 2n$, we have

$$e^{-\rho}\rho^{2n} \rightarrow e^{-2n}(2n)^{2n} e^{-\frac{\alpha^2}{4n}} \qquad (18)$$

Thus the standard deviation, $\Delta\rho$, of ρ is only $\sqrt{2n}$. The relative width, $\Delta\rho/\rho$, of the distribution becomes smaller with increasing n:_The electron is practically confined to a circle on the XY plane for large n (when $m = l$ and $l = n - 1$.) It is interesting to calculate the energy associated with radial motion in this case. (One does not expect any from a strictly classical stand point.) There are two ways of calculation:

(i) One may subtract the energy $\frac{l(l+1)\hbar^2}{2\mu r^2}$, linked to angular motion, from $|E|$ which is just the total kinetic energy in both classical and quantum mechanics. Setting $l = n - 1$ and using the appropriate value of r viz. $r = \frac{\rho}{2\eta} = \frac{n}{\eta}$ we obtain

$$(E)_{radial} = \frac{|E|}{n} \qquad (19)$$

(ii) One may, alternatively, use the uncertainty relation to first compute Δp_r from $\Delta r = \frac{\Delta\rho}{2\eta}$; and then calculate $(E)_{radial}$ via $(E)_{radial} = \frac{(\Delta p_r)^2}{2\mu}$. Thus

$$(E)_{radial} \approx \frac{4\hbar^2\eta^2}{2\mu(\Delta\rho)^2} \approx \frac{|E|}{n} \qquad (20)$$

- ***l* = *n* – 2**

The primary aim of this work is to establish the connection between the size of the major axis ($2a$) and the principal quantum number (n): For a given nucleus (having charge Ze) the energy of the system depends only on 'a' in classical mechanics while it depends only on the principal quantum number 'n' in quantum mechanics. Remember that the major axis joins the point in the orbit where the radial distance of the electron from the force-centre (nucleus) is least to the point where the radial distance from the nucleus is most; it is also called the apsidal line. As r does not change for small changes in the direction of the radius vector near the major axis, the electron spends relatively longer periods of time at the ends of the apsidal line. Since there is no analogue of the Runge-Lenz vector in quantum mechanics (unless one thinks of superposition of states or deals with wave-packets), distances to the two ends of the major axis may be ascertained by finding the distances to the two maxima of $R_{nl}^2 r^2$ at which it has the two highest values.

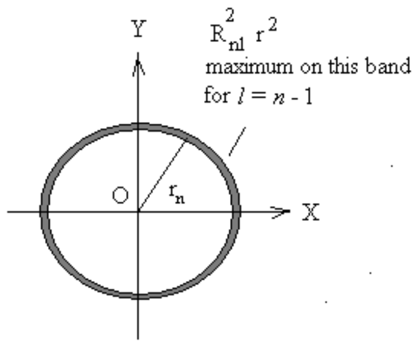

Fig. 1

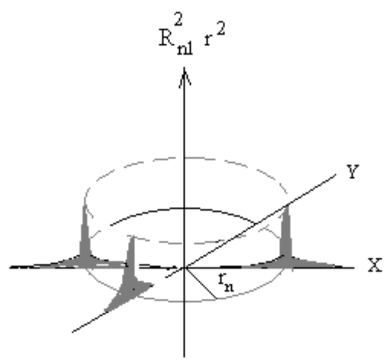

Fig. 2

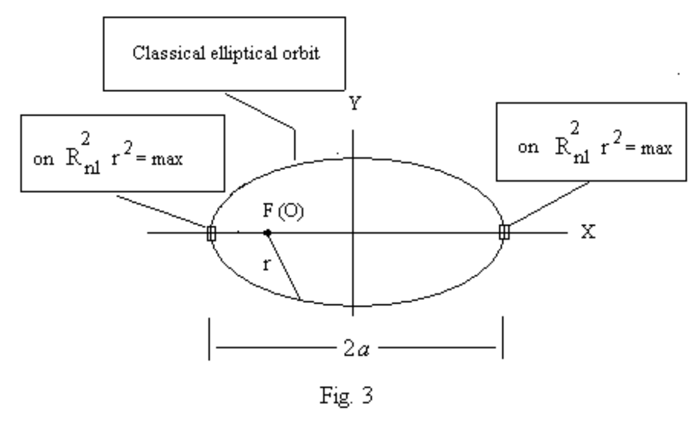

Fig. 3

Fig.1. For $l = n - 1$, $R_{nl}^2 r^2$ has its maximum value at $r = r_n = \frac{n}{\eta}$. The distribution has a width of approximately $\frac{\sqrt{2n}}{\eta}$.

Fig.2. A three-dimensional version of Fig. 1.

Fig.3. For $l \leq n - 2$, $R_{nl}^2 r^2$ has two or more maxima. The values of r at which $R_{nl}^2 r^2$ has its two highest magnitudes lie at the ends of the major axis.

In fact, these correspond to the largest and the smallest values of r at which $R_{nl}^2 r^2$ have its maxima. Note that the number of maxima of $R_{nl}^2 r^2$ is $(n - l)$. In between two successive maxima of $R_{nl}^2 r^2$ there is always a minimum of $R_{nl}^2 r^2$ where the function also goes to zero. Notice that we are relating maximum time spent to maximum of $R_{nl}^2 r^2$, presumably a sensible guess.

For $l = n - 2$,

$$L_{n+l}^{2l+1}(\rho) \rightarrow L_{2n-2}^{2n-3} = (2n-2)![\rho - (2n-2)] \qquad (21)$$

Thus

$$R_{nl}^2 r^2 \sim e^{-\rho}[\rho^n - (2n-2)\rho^{n-1}]^2 \qquad (22)$$

The maxima of $R_{nl}^2 r^2$ are located at

$$\rho_{\pm} = (2n-1) \pm \sqrt{4n-3} \approx 2n \pm 2\sqrt{n}, \qquad (23)$$

while there is a minimum at $\rho = (2n - 2) \approx 2n$. Arguments advanced above lead to a length of the major axis equal to $\frac{(\rho_+ + \rho_-)}{2\eta} \approx \frac{2n}{\eta}$. Going back to the expression for the energy in classical mechanics, we find that such a length of the major axis leads to the correct value of the energy. Thus our expectations are fulfilled for $l = n - 2$.

- ***l* = *n* – 3**

Here

$$L_{n+l}^{2l+1} \rightarrow [(2n-3)!]^2[-\frac{1}{2!(2n-5)!} + \frac{\rho}{(2n-4)!} - \frac{\rho^2}{(2n-3)!2!}] \qquad (24)$$

Hence the roots (and minima) of $R_{nl}^2 r^2$ are at

$$\rho = (2n-3) \pm \sqrt{(2n-3)} \qquad (25)$$

To find where the maxima of $R_{nl}^2 r^2$ lie, let us put $\rho = (2n-2)+\alpha$. The equation satisfied by α is

$$\alpha^3 - (10n-12)\alpha - (12n-16) = 0 \qquad (26)$$

Following Cardan [Hall and Knight, loc cit] let us set α = $y + z$ and require: $yz = \frac{(10n-12)}{3}$.
Then

$$y^3 = 2(3n-4) + \sqrt{4(3n-4)^2 - \frac{(10n-12)^3}{27}} \qquad (27)$$

$$z^3 = 2(3n-4) - \sqrt{4(3n-4)^2 - \frac{(10n-12)^3}{27}} \qquad (28).$$

When n is large

$$y \approx e^{\frac{\pi i}{6}} (\frac{10n}{3} - 4)^{\frac{1}{2}} (1, \omega, \omega^2) \qquad (29a)$$

and

$$z \approx e^{\frac{-\pi i}{6}} (\frac{10n}{3} - 4)^{\frac{1}{2}} (1, \omega, \omega^2) \qquad (29b)$$

where $(1, \omega, \omega^2)$ are the cube roots of unity (1).
For large n the required solutions are

$$\alpha_1 \approx \sqrt{(\frac{10n}{3} - 4)}\, [e^{\frac{\pi i}{6}} . + e^{\frac{-\pi i}{6}}] = \sqrt{3(\frac{10n}{3} - 4)} \qquad (30a)$$

$$\alpha_2 \approx \sqrt{(\frac{10n}{3} - 4)}\,[e^{\frac{\pi i}{6}}.\omega + e^{\frac{-\pi i}{6}}.\omega^2] = -\sqrt{3(\frac{10n}{3} - 4)} \qquad (30b)$$

$$\alpha_3 \approx \sqrt{(\frac{10n}{3} - 4)}\left[e^{\frac{\pi i}{6}}\omega^2 + e^{\frac{-\pi i}{6}}\omega\right] = 0 \qquad (30c)$$

The sum of the largest and the smallest values of ρ viz. ($\rho_1 + \rho_2$) is approximately equal to 2(2n – 2) or 4n, when n is large. The length of the major axis, by our assumption, is then $\frac{2n}{\eta}$ and we are again led to the conclusion that the energy E depends on this particular quantity.

- $\boldsymbol{l = n - 4}$

In this last algebraically solvable case

$$L_{n+l}^{2l+1} \rightarrow -[(2n-4)!]^2[\frac{1}{3!(2n-7)!} - \frac{\rho}{2!(2n-6)!} + \frac{\rho^2}{(2n-5)!2!} - \frac{\rho^3}{(2n-4)!3!}] \qquad (31)$$

The minima of $R_{nl}^2\, r^2$ are placed at $\rho = (2n-4) + \alpha$, where α is a solution of the cubic equation

$$\alpha^3 - 3(2n-4)\alpha - 2(2n-4) = 0 \qquad (32)$$

The required values of α can be obtained by Cardan's method. For large n the solutions are

$$\alpha_1 \approx \sqrt{(2n-4)}\,[e^{\frac{\pi i}{6}}. + e^{\frac{-\pi i}{6}}] = \sqrt{3(2n-4)} \qquad (33a)$$

$$\alpha_2 \approx \sqrt{(2n-4)}\,[e^{\frac{\pi i}{6}}.\omega + e^{\frac{-\pi i}{6}}.\omega^2] = -\sqrt{3(2n-4)} \qquad (33b)$$

$$\alpha_3 \approx \sqrt{(2n-4)}\left[e^{\frac{\pi i}{6}}\omega^2 + e^{\frac{-\pi i}{6}}\omega\right] = 0 \qquad (33c)$$

To find the values of ρ where $R_{nl}^2 r^2$ has its maxima, let us put ρ = (2n-3) + β . Some algebraic manipulations lead to the following equation for β :

$$\beta^4 - 6(3n-5)\beta^2 - 8(5n-9)\beta + (24n^2 - 126n + 153) = 0 \qquad (34)$$

Collecting the leading terms (remember that we are interested in the large n situation) we have

$$\beta^4 - 18n\beta^2 - 40n\beta + 24n^2 = 0 \qquad (35)$$

This equation can be solved by the technique invented by Descartes [Hall and Knight, loc cit]. For pedagogical reasons we give a brief outline of the method. Consider the equation

$$x^4 + qx^2 + rx + s = 0 \qquad (36)$$

Assume

$$x^4 + qx^2 + rx + s = (x^2 + kx + l)(x^2 - kx + m) \qquad (37)$$

Then by equating coefficients we get

$$k^6 + 2qk^4 + (q^2 - 4s)k^2 - r^2 = 0 \qquad (38)$$

This is a cubic equation in k^2. After solving this equation we can find the values of m and l. Finally x (four possible values) is obtained from the pair of equations

$$x^2 + kx + l = 0 \qquad (39)$$

and

$$x^2 - kx + m = 0 . \qquad (40)$$

Applying this technique to our equation for β, we get

$$\beta \approx \frac{\sqrt{28n} \pm \sqrt{28n - 4(5n - \frac{19\sqrt{n}}{5})}}{2} \;, \quad \frac{-\sqrt{28n} \pm \sqrt{28n - 4(5n + \frac{19\sqrt{n}}{5})}}{2} \qquad (41)$$

In the large n situation the highest and the lowest values of β are respectively $\frac{1}{2}(\sqrt{28}+\sqrt{8})\sqrt{n}$ and $-\frac{1}{2}(\sqrt{28}+\sqrt{8})\sqrt{n}$. Clearly the sum of the corresponding values of ρ is approximately equal to $4n$, as anticipated. Our stand is therefore vindicated.

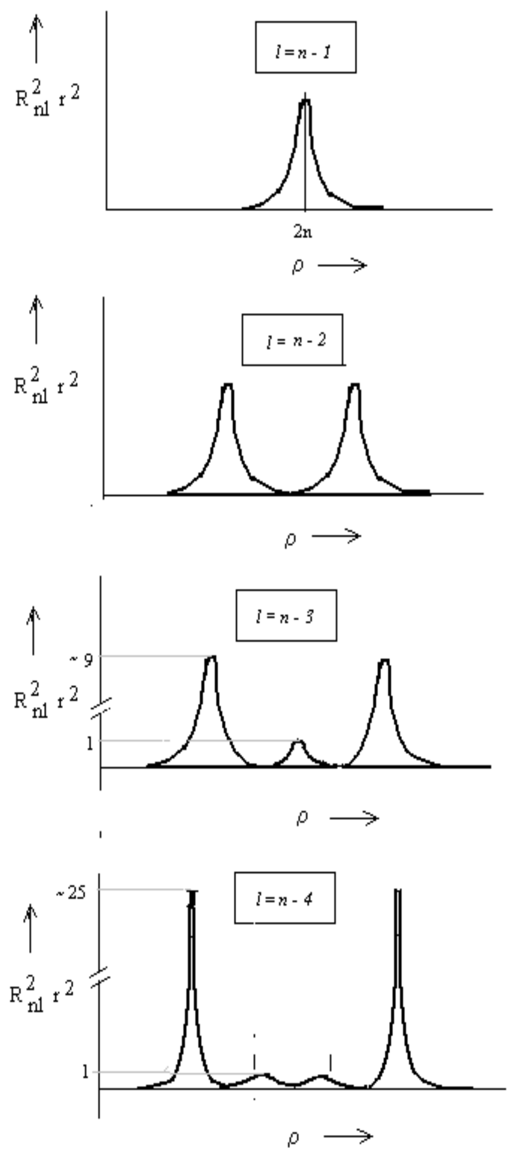

Fig. 4

Fig.4. Plots (schematic) of the variation of $R_{nl}^2 r^2$ with ρ for different values of *l*.

Conclusions

The cases for other '*l* 'values may be handled by numerical methods. However, the trend is evident, for it has to be consistent with Bohr's correspondence principle. We hope that through this article we have been able to illustrate how quantum effects disappear and classical results emerge in the limit of large '*n*' values. It may also help the students to accept quantum mechanics as a deeper and refined description of nature.

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